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THE USE OF AMMONIA AS A QUALITATIVE TEST FOR DETERMINING WHEN SOLID COPPER HAS COMPLETELY PRECIPITATED FROM AQUEOUS SOLUTIONS CONTAINING COPPER(II) IONS

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ABSTRACT

In this study, two methods were compared to efficiently determine the absence of copper ions from a copper(II) chloride dihydrate (37.274% copper by mass) solution after precipitation using solid magnesium. In one method, a solution color change from pale blue to colorless was used as indication of a completed precipitation of copper. In the alternative method, ammonia was added to aliquots of solution which indicated remaining copper ions with a royal blue complex. For both methods, magnesium turnings were added to a blue copper(II) chloride solution until it was determined, as indicated above, that all copper had precipitated from solution. Afterwards, any excess magnesium was reacted with concentrated hydrochloric acid. The solution was then filtered and the precipitate was washed, dried, and weighed. After ten trials per method, the average percent copper obtained, to a 95% confidence interval, was 34 ± 2% with ammonia testing and 22 ± 2% without it. An *F*-test indicated an equal variance between methods. The corresponding *t*-test value of 9.58, when compared to the two-tailed *t*-critical value of 3.20, indicated a statistically significant difference of data between the two methods.

Keywords: copper recovery, qualitative test, tetraamine copper(II) ion, general chemistry lab, undergraduate chemistry experiments.

INTRODUCTION

Many experiments performed in freshmen undergraduate chemistry labs require the students to precipitate copper metal from an aqueous solution containing Cu^{2+} ions after dissolution of samples that are initially in the solid state. Examples include laboratory experiments performed at Kansas State University (Dikeman 2005), Clark College (Department of Chemistry, Clark College 2011), and the University of California – Davis (Department of Chemistry, UC-Davis 2016). After retrieving the copper from solution the students are often asked to report the percentage of copper in an unknown mixture or compound or percent recovery, if the lab began with elemental copper. A common method used to determine when all the copper has precipitated from solution is visual inspection. Aqueous copper(II) ions, $[Cu(H_2O)_6^{2+}]$, will give the solution a pale blue hue. When the solution is colorless it is presumed to no longer have copper ions dissolved in it. This methodology, which is currently being employed by students at the University of North Georgia (Konzelman et al. 2014), can lead to inaccurate results as $[Cu(H_2O)_6^{2+}]$ has a low extinction coefficient, 12 $M^{-1}{\cdot}cm^{-1}$ (Figgis 1966) at a wavelength

of maximum absorbance that is outside the range of light visible to the human eye. As a result, the solution can appear colorless even when there may be significant concentrations of copper(II) ions left in solution, making it difficult to clearly determine when the precipitation of copper has been completed. If copper is left in solution, it cannot be collected, dried, and weighed. Thus, experimentally determined amounts of copper will be erroneously low. This is a particular problem in percent composition determinations of copper containing analytes when accuracy is of significant interest, as is the case at the University of North Georgia, where the students are asked to identify an unknown compound from their analyses. The inability to correctly assess when all of the copper has been removed from solution so that it may be collected, dried, and weighed has led to inaccurate results and correspondingly incorrect identifications of the unknown copper compounds.

In this study, a new method for detecting the presence of copper(II) ions in aqueous solution, to be incorporated into undergraduate chemistry experiments, was investigated. This new method is centered on the use of ammonia as an indicator to detect the presence of copper(II) ions in solution. Addition of ammonia to a solution containing Cu^{2+} causes the formation of the complex ion $[Cu(NH_3)_4^{2+}]$, tetraamine copper(II), according to Equation 1. Owing to a very high formation constant of the complex ion, $K_f = 1.1 \times 10^{12}$ (Harris 2016), effectively all of the copper in solution is in the form of tetraamine copper(II) once ammonia has been added. Furthermore, the presence of $[Cu(NH_3)_4^{2+}]$ is much easier to detect at lower concentration levels by visual inspection than is $[Cu(H_2O)_6^{2+}]$ because the absorption maximum has shifted from ~800 nm for the aqua ion to ~600 nm for the tetraamine copper(II) ion as a result of the stronger ligand field provided by the ammonia compared to water (Cotton and Wilkinson 1988). Testing small portions of the reaction solution during copper precipitation with the addition of ammonia has led to a more facile assessment of when copper precipitation is complete and more accurate determinations of copper content in solid samples.

$$Cu^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightarrow Cu(NH_3)_4{}^{2+}{}_{(aq)} \qquad \text{(Eq. 1)}$$

METHODS

Ten replicate trials were carried out using each method for the determination of complete copper precipitation described below. Microsoft Excel 2010 was used to run statistical analysis of the results.

Using color of the reaction solution to test for the presence of copper(II) ions in solution:

High purity (99+%) copper(II) chloride dihydrate, 1.0 to 1.3 g, was weighed into a beaker and dissolved in 50 mL of distilled water and 5 mL of 6 M hydrochloric acid to create a blue solution. Two to five magnesium turnings were added at a time with rapid stirring until copper precipitation was completed, as indicated by a colorless solution. Several more milliliters of the hydrochloric acid were added to react with excess magnesium until the addition of more acid no longer resulted in gas evolution from the solution (release of hydrogen). The elemental copper was then collected using a funnel and filter paper, and washed with water multiple times. Afterwards, the funnel was moved to another flask where the contents were washed three times each with ethanol

and then acetone. The copper and filter paper were placed on a watch glass in a 100 °C oven to dry until successive weighing indicated no significant change in sample mass (less than 2 mg). The copper was allowed to cool to room temperature before a final mass was taken.

Using ammonia to test for the presence of copper(II) ions in solution:

The formation of aqueous copper(II) chloride solutions and precipitation of copper was carried out as above. Once the reaction solution appeared colorless, three or four drops of the solution were placed in a small test tube. A 1-mL aliquot of 6 M ammonia was then added to and mixed with the solution in the test tube. In instances where a royal blue color was observed in the test solution the copper precipitation reaction was allowed to continue with additional magnesium, as required. Once the test solutions no longer revealed a royal blue color, the precipitation reaction was halted. Excess magnesium was then dissolved and the elemental copper was collected, purified, and weighed as described above.

RESULTS

Repeat measurements were carried out with and without using the qualitative ammonia test and the results are summarized in Table I. Mean values for the experimentally determined percentage of copper in the original copper(II) chloride dihydrate samples were calculated for both methods and uncertainties were determined for n = 10 at the 95% confidence interval. The average experimental percent copper obtained from using visual inspection of the reaction mixture to determine when the precipitation reaction should be stopped was 22% ± 2%, with the experimental values ranging from 19.16% to 26.98%. Whereas, the average percent copper obtained experimentally using the addition of ammonia as a qualitative test for the presence of copper in solution was 34% ± 2%, with the measurements ranging from 30.16% to 37.18%. Percent recovery values and ranges are reported as a percentage of the theoretical mass of copper in the initially weighed samples of $CuCl_2 \cdot 2H_2O$.

Table I. Summary of copper recovery results from aqueous solutions of copper(II) chloride

	Results Without Using the Qualitative Ammonia Test	Results Using the Qualitative Ammonia Test
Average % Copper	21.6	34.45
Average % Recovery	57.95	92.42
% Recovery Range	51.4%–72.4%	80.9%–101.2%
% Copper Standard Deviation	3.02	2.99

Statistical tests were carried out on the measurements to compare the results from the two methods. An *F*-test was performed using the variances from each method and $F_{calculated}$ was determined to be 1.026. The details of the *F*-test are given in Table II. A *t*-test for two samples with equal variances performed on the two sets of data resulted in a $t_{calculated}$ value of 9.58 compared to the $t_{critical}$ two-tailed value of 3.20. The details of the *t*-test are given in Table III.

Table II. Summary of the *F-Test* for comparison of method variances

	Variable 1	*Variable 2*
Mean	34.45	21.60
Variance	8.88	9.11
Observations	10	10
Degrees of Freedom	9	9
F	1.026	
F Critical One-tail	3.179	

Table III. Summary of the two-sample *t*-test: assuming equal variances at the 99.5% confidence interval

	Variable 1	*Variable 2*
Mean	34.45	21.60
Variance	8.88	9.11
Observations	10	10
Pooled Variance	8.99	
Degrees of Freedom	18	
t Stat	9.58	
t Critical Two-tail	3.20	

DISCUSSION

The experimental methods were chosen to be consistent with procedures currently carried out by general chemistry students at the University of North Georgia. Well characterized samples of $CuCl_2 \cdot 2H_2O$ were used in place of the unknown compounds given to the students for purposes of assessing the accuracy of the two methods. In order to isolate the copper from the compound, solid samples were first dissolved into acid to produce a blue solution (Figure 1). Elemental copper was then precipitated out of solution through a metal displacement reaction carried out by the addition of magnesium metal (Equation 2). Once it was determined that the copper was

$$Cu^{2+}{}_{(aq)} + \ Mg_{(s)} \rightarrow \ Mg^{2+}{}_{(aq)} + \ Cu_{(s)} \qquad \text{(Eq. 2)}$$

all removed from solution, by either method, excess HCl was added to completely dissolve any solid magnesium remaining in the reaction mixture (Equation 3) so that it would not be collected with the solid copper and generate falsely high results.

$$2\,HCl_{(aq)} + \ Mg_{(s)} \rightarrow \ MgCl_{2\,(aq)} + \ H_{2\,(g)} \qquad \text{(Eq. 3)}$$

Since hydrogen gas is evolved in the reaction between magnesium and hydrochloric acid, the cessation of bubbling in the reaction mixture was used as an indicator that the magnesium had all dissolved. After the magnesium had been separated from the solid copper in this manner, the copper metal was filtered from solution, cleaned, dried, and weighed as described in the methods.

The method commonly used to determine when copper has completely precipitated from solution is the disappearance of the blue color in solution to produce a colorless solution as seen in Figure 2. This, however, can be inaccurate as seen in Figure 3, which shows the results from adding concentrated ammonia to small aliquots of the reaction mixture during the course of the precipitation reaction. The test tube on the far left in Figure 3 is the result of adding ~1 mL of 6 M ammonia to a few drops of the reaction solution once it had gone colorless. The deep blue color indicates that there is still copper present in solution, now in the form of the $[Cu(NH_3)_4{}^{2+}]$ complex. The remaining test tubes show the progression of the results from the ammonia test, from left to right, as the metal displacement reaction was allowed to continue. The test tube on the far right is representative of when the copper precipitation reaction was determined to be complete according the ammonia test. While the visual results from

adding ammonia to the reaction solution can still be slightly ambiguous, the use of this test yields much more accurate results than the visual inspection of the reaction mixture itself, as will be discussed below.

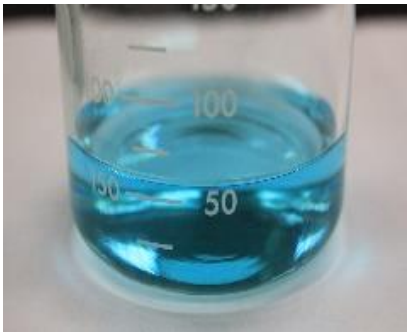

Figure 1. Blue solution of $CuCl_2 \cdot 2H_2O$.

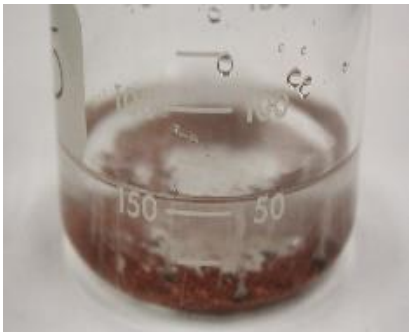

Figure 2. Solution of $CuCl_2 \cdot 2H_2O$ that has gone colorless due to the precipitation of copper by the addition of magnesium metal.

Figure 3. Ammonia test results over the course of the copper precipitation reaction.

Copper(II) chloride dihydrate has a formula weight of 170.5 amu and a theoretical percent copper of 37.27%. Comparing the mean values for percent Cu obtained from each method to this value (Figure 4), it can be seen that the new method involving the formation of the deeply colored $[Cu(NH_3)_4^{2+}]$ complex to detect copper ions in solution during the isolation reaction yields considerably more accurate results. Visual inspection of the reaction solution yielded a 42% error; whereas, the new method resulted in a considerably lower percent error of 7.6%. Additionally, it can be seen in Table I that the percent recovery for copper was significantly higher when using the qualitative ammonia test. On average, 92% of the theoretical amount of copper was recovered when using this test compared to an average of 58% without it. Finally, when the mean value for percent copper and Equation 4 are used to calculate an experimental formula weight from each method, the new method results in a formula weight of 184 amu compared to 294 amu obtained using the method of visually inspecting the reaction solution for loss of color. Clearly, the method of visual inspection, which is currently in use, is less accurate and would more likely lead to incorrect identification of unknown compounds based on formula weight.

$$\text{Formula weight} = \frac{Atomic\ Mass\ of\ Copper \times 1\ Copper\ atom\ /\ unit}{\%\ Cu} \qquad \text{(Eq. 4)}$$

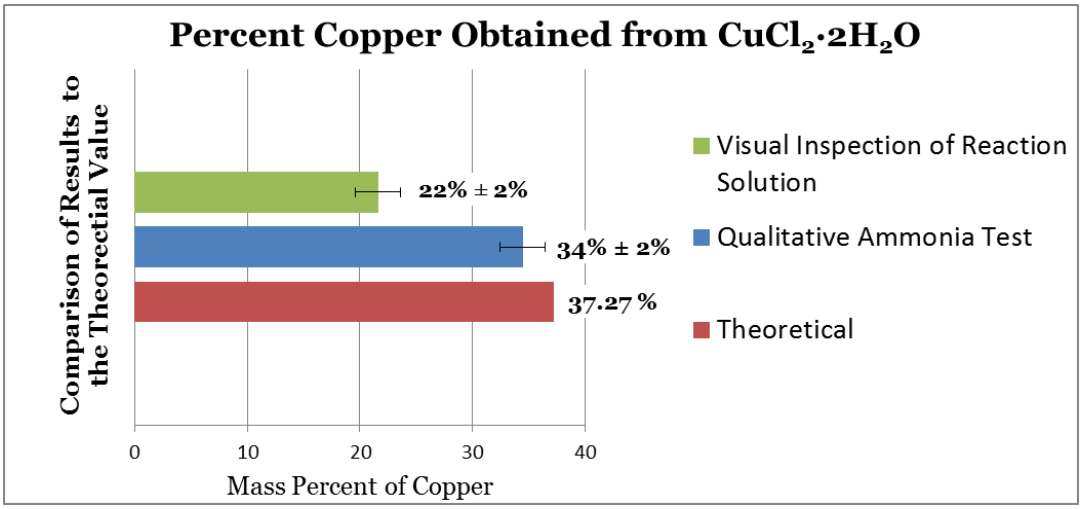

Figure 4. Percent copper in copper(II) chloride dihydrate: theoretical value compared to experimentally determined values using both methods for determination of complete copper precipitation.

Not only is the new method more accurate but statistical analysis indicates that the mean values for percent copper determined by each method are statistically different from one another. The $F_{calculated}$ value of 1.026 is less than the $F_{critical}$ value of 3.18 with 9 degrees of freedom indicating that the variances for the data generated by the two methods are equal within a 95% confidence interval. This allowed for the performance of a two tailed student's *t*-test comparing the two methods with equal variances. The results of the *t*-test indicate that the two methods are statistically different to the 99.5% confidence interval as the $t_{calculated}$ value of 9.579 is much greater than the $t_{critical}$ value of 3.20. This means that there is less than a 0.5% probability that these two methods resulted in the same experimentally determined value within experimental error.

While the new method employing ammonia as a qualitative indicator for the presence of copper in the reaction solution has a much greater accuracy than the method currently in use, it still does not yield results that are in agreement with the known value. The theoretical percent Cu of 37.3% lies just outside the 95% confidence interval for this method (34% ± 2%). A likely cause of error is improperly differentiating between a light blue and colorless ammonia test result, the last two test tubes on the right in Figure 3, causing the continuation of the experiment while small amounts of copper remained in solution. However, this new method should allow students to obtain more accurate results and to more readily identify unknown copper compounds based on experimentally determined percent copper and formula weight values. In addition, this new method only requires the addition of inexpensive and readily available aqueous ammonia and does not overly complicate the pre-existing methodology.

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